PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Ladle and method for the Treatment of Molten Metals

We, L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE, a Company organized under the laws of France, of 75, Quai d'Orsay, Paris (France), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a ladle specially adapted for treating molten metals by gas blowing. More specifically, it is concerned with the design and the operation of a ladle suitable for the methodical activation of metallurgical reactions and exchanges within a molten metallic bath and at its surface, by stirring said bath by means of a gas stream blown into the molten mass across one or several refractory porous elements inserted in the bottom of the ladle containing this molten mass.

One object of the invention is to achieve very active and methodical agitation of a molten metallic bath with a minimum quantity of gas.

Another object is to improve the efficiency and rapidity of metallurgical treatments in which a molten metal is brought in contact with a reagent such as, for instance, a slag, or a chemically active gas injected in the upper part of the molten bath.

A further object of the invention is to allow for such treatments to be carried out conveniently and economically in a pouring ladle of the conventional bucket shape, with or preferably, without external heating. It is contemplated that this treatment can also be carried out during the transfer of such a ladle.

Yet another object of the invention is to improve the possibility for an economical use in the metallurgical field of gases such as helium and argon which are relatively costly, so that their industrial use in metallurgical treatments has often been considered with some hesitation, in spite of their recognized technical advantages.

Subsidiarily, the invention still has the object of facilitating the production of metals in a very homogeneous condition, accurately adjusted to predetermined standards, and to reduce the waste, as by oxidation or nitride formation, of costly ingredients, such as for instance magnesium or boron, when such elements are added to the bath in the preparation of special products like nodular iron or boron steel.

Finally, a last object of the invention is to bring down the cost of equipment, operations and maintenance whenever active stirring of a bath of molten metal is required.

The prior art discloses a variety of devices for agitating a metallurgical fused bath in order to promote exchanges and reactions within said bath at its surface. Stirring may for instance be achieved mechanically, as in a rotating mixer, or by electromagnetic action. It may also be obtained by gas blowing, as in a Bessemer converter. However, the flow of gas in a Bessemer converter is necessarily several hundred times large than that which has been found suitable according to the present invention, for achieving the purpose stated in the foregoing. Whereas the gas flow in a Bessemer converter may be for instance around 10,000 liters per minute and per ton of metal, the present invention provides positive means to control the effects of the gas injected into the fused bath, in order to achieve very effective stirring by a very small gas flow, which may be for instance comprised between 5 and 25 liters per minute per ton of metal, depending on the weight of the batch of metal treated.

In the course of actual tests with ladles of increasing sizes, the applicants have equipped these ladles with porous plugs of various sizes, including some which were quite small in proportion to the ladle size, so that the area of the plug, contacting the molten material, was smaller than 1/25 of the top bath surface. This surface ratio could be further decreased for instance to 1/100 or less as the ladle size increased, and yet very effective stirring could be obtained, while the gas flow could be kept down to the very small values mentioned hereabove. It appears therefore that the ratio

between the surface of the porous element and the top bath surface, is a critical factor in obtaining the desired results.

Further critical factors, which are correlative with the above factor, are the ratio between the depth of the molten bath and its horizontal dimensions, and the gas-permeability of the porous element.

According to the present invention, there is provided a ladle for the treatment of molten metals by gases, with a refractory lining, the bottom of which comprises a porous portion substantially flush with the rest of the bottom lining, the ratio (a) between the ladle depth at its normal filling level and the ladle's inner diameter at said level being comprised between 1 and 1.8 and the ratio (b) between the porous area s and the area S of the ladle inner section at its normal filling level complying with the relation:

$$0.32 \log S + 0.39 < \log s < 0.67 \log S - 0.14$$

In a preferred form of the invention, the ratio (a) is comprised between 1.2 and 1.6, a preferred value being 1.5, while the ratio (b) complies with the relation:

$$0.475 \log S < \log s < 0.475 \log S + 0.40.$$

The base of the logarithms used in the foregoing and following formulæ is the decimal base, S and s being expressed in square centimeters.

According to another feature of the invention, the porous portion of the bottom of a ladle of the type specified should have a gas permeability comprised between 50 and 200 liters of air issuing at room temperature and normal atmospheric pressure per minute, per square decimeter of exposed porous area, and per kilogram per square centimeter upstream pressure. It should be indicated, in this respect that for a given pressure, the gas quantity actually delivered per minute into molten steel or iron will be only about 1/5 to 1/3 of the above indicated quantities, since the gas will be fed through narrow pores having their walls at temperatures for which the gas viscosity is high. For instance, the viscosity of argon increases from 220 micropoises at 20° C. to 563 micropoises at 827° C., and that of helium from 194 micropoises at 20° C. to 471 at 817° C.

A further feature of the ladle according to the present invention, in view of its use for the treatment of ferrous metals, is that the porous portion is a removable silicon carbide plug, which is preferably sealed to the ladle lining by means of chromium-oxide base cement containing a small amount of bentonite and sodium silicate. Although other refractory porous materials may be satisfactory, silicon carbide is advantageous because it has a tendency to be dissolved very slowly in molten ferrous metal, resulting in a favourable effect, similar to a pickling action, owing to which there is much less clogging of the pores than with other porous materials. However, the rate of this dissolution is slow enough to allow the plug to be used for several operations in succession, account being taken of the fact that the plug permeability decreases gradually during the plug life.

The porous plug may have a thickness similar to that of the usual refractory linings of metallurgical vessels, for instance between 8 and 20 centimeters, more commonly from 10 to 15 centimeters, and should best have an apparent porosity, in volume, comprised between 20 and 40%, a preferred range being from 25 to 35%, while its lacunary volume should be, for its larger part, namely 60 to 80%, formed of pores having an equivalent diameter from 30 to 80 microns, this equivalent pore diameter being for instance measured by the mercury capillary pressure test. The remainder of the lacunary volume may comprise smaller fractions formed of pores having equivalent diameters in the ranges 10 to 30 microns and 80 to 120 microns.

Very satisfactory results have been obtained with a porosity of 30%, with the above distribution of pore sizes. The gas pressure, being the excess over the hydrostatic head of molten metal, is advantageously kept below 3 kg/cm², the preferred range being from 0.15 to 1.5 kg/cm². Under the above permeability conditions, it has been observed, when blowing argon into molten pig iron, that the gas flow, per square decimeter of porous area, varied from 5 to 50 liters per minute, approximately, as the pressure rose from 0.15 to 1.5 kg/cm², this gas flow being measured at room temperature and normal atmospheric pressure, by means of a flowmeter. When testing the permeability of the same porous material at room temperature, the gas flow was found approximately 4 times larger, since the viscosity of the gas when coming out of the porous material was substantially less in the latter case.

The ladle according to the invention appears particularly advantageous for the treatment of molten ferrous metals by stirring said metals together with a slag, specially when said slag is added in the solid state to the molten metal. Slags in granular form, such as for instance granulated lime, react much more effectively with molten iron or steel when the bath is stirred by means of a ladle according to the invention.

Desulphurization of molten iron or steel is advantageously carried out, according to the invention, by using a strongly basic slag,

which may be charged in the solid state into the ladle, before filling the ladle with molten metal. Blast furnace slags are also advantageously used for this purpose. These slags may, or not, be themselves previously desulphurized, according to the relative sulphur contents of the slag and metal. Preferably, the slag should become very fluid at the operating temperature.

A great advantage of the gas insufflation practised according to the invention, is its effectiveness for promoting the double reaction of desulphurization:

$$CaO + Fe\,S \rightarrow Ca\,S + Fe\,O$$
$$Fe\,O + C \rightarrow CO + Fe$$

The injected gas lowers the partial pressure of CO, and assist the removal of CO from the bath, thereby activating the above double reaction.

A similar effect may be achieved when applying the gas injection according to the invention for assisting the de-oxidation of steel by a small addition of carbon before pouring. The gas injection activates the dispersion of carbon and lowers the partial pressure of CO. If a monoatomic gas is used, nitrogen may also be simultaneously eliminated from the molten metal.

The same effect may also be put to use for assisting the elimination of silicon in the following way: recent tests have shown that silicon becomes at first oxidised into monoxide SiO, which has a fairly high vapour pressure in the range of temperatures prevalent in metallurgical processes. By lowering the partial pressure of gaseous SiO, its elimination is activated.

The invention will now be further described in connection with the appended drawing, in which:

Figure 1 is a vertical cross-section of a pouring ladle according to the invention.

Figure 2 is a chart indicating the preferred values in function of the bath top area, of the area of the porous element, and of the diameter of this porous element, when circular. It also indicates these data in function of the weight of the treated charge, when this charge is composed of ferrous metals.

Figure 3 is a chart indicating the variations of the gas flow, also in function of the weight of a batch of ferrous metal.

The pouring ladle represented in Figure 1 is of the usual bucket shape which the applicants have found quite appropriate for their purpose. This ladle is provided with a porous element 1 inserted in the bottom lining and connected to a gas cylinder 2 through a pressure regulator 3, a pressure gauge 4, a flowmeter 5, a pipeline 6 and a gas chamber 7. It will be noted that the porous element 1 offers a very small section, in proportion to the size of the ladle. The porous element may advantageously be located in the center of the ladle bottom. However, good results have also been obtained with a plug located slightly off-center. In any case, the plug top should be substantially flush with the lining surface. The lining of the ladle bottom is joined with the side wall lining by a fillet having a fairly large curvature radius. The ladle depth should be sufficient to hold a depth of metal about 1.5 times the mean diameter of the ladle, which has a frusto-conical shape as illustrated. This feature is in contradistinction to the usual feature of vessels employed heretofore in the metallurgical operations to which the present invention is applicable, such as, more particularly, the desulphurizing of ferrous metals, for which very shallow vessels are usually recommended. When compared to such shallow vessels, a ladle according to the present invention offers a series of advantages which are specially valuable when the tonnage of the molten bath is a large one. They include the possibility to use standard equipment, as generally available in metallurgical plants, with only slight and inexpensive modifications, since a pouring ladle of the conventional frusto-conical shape may be quite suitable when fitted with the gas-blowing apparatus described.

A deep ladle also has the advantage of being more easily and effectively provided with an air-tight lid, than a very wide and shallow vessel would be. Such a lid is useful to protect the bath from atmospheric contamination, and is necessary when it is desired to operate at sub-atmospheric pressures. Even without a lid, atmospheric contamination is reduced when using a deep ladle, since the metal surface exposed to the atmosphere is restricted. For the same reason, heat losses are reduced, while this type of ladle is particularly easy to handle, and quite appropriate for carrying out a metallurgical treatment during the transfer of the ladle, if so desired, since the gas-blowing apparatus may remain attached to the ladle.

Owing to the very small size of the porous plug, it is comparatively easy to maintain a gas-tight joint between the side walls of this plug and the surrounding refractory lining. Consequently, there is no loss of gas. Also, the invention allows for the use of a small gas pressure, exerting negligible stress on the plug assembly.

The practical range for the plug diameter is approximately from 5 to 25 centimeters, this being the diameter of the smaller base of the plug when the shape of this plug is made frusto-conical, so as to facilitate its insertion into and removal from the ladle bottom. It has been found, for instance, that a plug of 10 centimeters diameter, which had given

satisfactory results when stirring a small batch of iron, of ½ ton, was also quite effective for stirring batches of 10 to 15 tons of iron, while the gas flow, per minute and per ton of metal, could be reduced without impairing the stirring activity as the tonnage increased.

The chart, Figure 2, indicates the minimum and maximum values between which the plug area s should best be kept, in function of the area S of the ladle inner section at its normal filling level, according to the formulas:

$$0.32 \log S + 0.39 < \log s < 0.67 \log S - 0.14$$
and
$$0.475 \log S < \log s < 0.475 \log S + 0.40,$$

the latter formula indicating the preferred limits, shown by the dotted lines of the chart, these limits being particularly satisfactory when the depth of the molten metal bath in the ladle is approximately 1.2 times the diameter of its surface. It is also possible to read, from this chart, the approximate weight of ferrous metal corresponding to a given bath surface, when the above depth-to-width ratio is 1.2. The chart also carries a scale where the plug diameter may be read directly, when the plug is circular in section. This plug diameter d may also be calculated in function of the weight T, according to the formula:

$$0.78 + 0.1 \log T < \log d < 1.1 + 0.2 \log T$$

which corresponds approximately with the values indicated in the chart Figure 2, when d is calculated in centimeters, and T in metric tons. It should also be noted that the plug diameter should be decreased, as the bath depth, and therefore the bath tonnage is increased, in a given ladle, assuming that the top area of the bath remains the same. This is due to the fact that the gas stream spreads laterally to some extent, as it rises, and therefore stirs a larger fraction of the bath top surface when the bath depth increases. The relation between the plug diameter d and the bath depth may, for all practical purposes, be taken approximately as inversely proportional, assuming that the bath top area is constant.

The chart, Figure 3, indicates, in function of the bath tonnage T, the various values of the gas flow F, in liters per minute and per ton of material treated, this flow being calculated at room temperature and normal atmospheric pressure. The line I shows the maximum values, beyond which excessive spitting, or projections of molten material might take place when the shape of the ladle complies with the above specifications and the line II shows the minimum values, for which a useful stirring effect begins to appear. These two lines correspond to the upper and lower limits of F according to the formula:

$$0.43 - 0.13 \log T < \log F < 1.56 - 0.384 \log T$$

which applies more particularly when the plug diameter is related to the bath tonnage according to the relation indicated hereabove.

The preferred range of permeability of the porous plug has been indicated hereabove by combined reference to its apparent porosity, in volume, and its pore-size distribution. This expression of the permeability has the advantage of being independent of the gas pressure, but it should be understood that equivalent expressions of the permeability might be formulated by having reference to other standard methods of permeability determination.

By way of example, a gas flow of 36 liters per minute, through a porous plug of 10 centimeters diameter, under a pressure of 1.4 kg/cm^2, has been found effective to stir a load of 2 tons of steel, the agitation being very lively, almost excessive. When reducing the gas flow to 16 liters/minute, under a pressure of 1 kg/cm^2, stirring was quite satisfactory. In a similar test, with a 3 tons load, a flow of 36 liters/minute, i.e. 12 liters/minute/ton, gave very lively agitation, which was found appropriate to achieve very quickly a high rate of sulphur removal when stirring molten steel in presence of a basic slag.

As an explanation for the critical effect of the factors selected according to the invention, it might be reasonably assumed that the stirring of the molten bath in the present invention is obtained mostly by convection currents, rising in the central zone of the bath, directly above the porous plug, and returning down in the annular exterior zone. This is in contradistinction to what takes place, for instance, when gas is blown into molten metal from above through a lance, under a pressure of from 7 to 10 kg/cm^2, the stirring being then mostly effected by the kinetic force of the projected gas, whereas the convection currents observed in the ladle of the present invention appear to be simply induced by the ascensional force of the gas, increased by the thermal expansion of said gas. The downward current appears to be merely a return current, along the free path provided around the central zone, since the gas injection is limited to this central zone. In support of this belief, it will be mentioned that the production of red fumes which has sometimes been observed when refining blast-furnace iron by the oxygen lancing method may be greatly reduced by simultaneously stirring the molten iron in a ladle of the type

described. It appears that all portions of the fused bath, including the lowermost layers, are subjected to the action of the gas stream and are successively brought into contact with the slag or other reagent present on top of the molten metal. Alternatively, the same portions of the molten metal mass are never left too long in contact with the top reagent, thereby avoiding over-oxidation of the metal, in the oxygen lancing procedure, and diminishing losses of metal and alloy elements, as evidenced by the diminution of red fumes; it has also been observed that the difference in the carbon content near the surface and at the bottom of the bath was much smaller when using the apparatus of the invention.

It will be understood that a circulation effect, similar to that obtained by the present stirring device, could not be secured if gas bubbles were rising from the entire surface of the vessel bottom, as suggested in prior disclosures.

When compared to known methods in which stirring is achieved by gases evolved through a reaction within the molten bath, the present invention offers the following advantages:

The action of the gas can be much more accurately controlled and adjusted, since the rate of blowing, the moment of blowing, the duration of blowing, and the chemical composition of the gas can be determined exactly at the operator's will. On the contrary, when one has to rely on a chemical reaction to evolve the gas, the speed of this reaction may be difficult to control, and the choice as to the gas composition is very limited. Also, when the reaction has started, the said reaction is difficult or impossible to control and stop. The thermal effects of such a reaction may also be found difficult to adjust, whereas the thermal effects of the gas used with the present device may be kept down to a minimum, and in any case may be easily calculated in advance, specially when the gas employed is chemically inert. It should be noted that no chemical reaction within the fusion bath could evolve the monoatomic gases which are often advantageously used with the present apparatus, namely argon and helium.

When compared to the "lancing" procedure, already referred to, from the stirring point of view, the method using the device of the invention achieves a better stirring efficiency while using much less gas, since the usual gas flow in the lancing procedure may be for instance averaging 120 liters/minute/ton. The present apparatus also avoids exposing the operator to the heat of the incandescent metal, as when handling the lance from above the fusion bath.

The invention also presents the advantage of achieving the production of fully degassed metal in a single operation, since it is no longer necessary to carry out a first treatment, in which the metal is stirred with a slag or other refining agent, followed by a degassing treatment. This is also a factor of large savings in equipment and operation costs, since the need for auxiliary furnaces, such as slag melting furnaces, can be eliminated.

Further, since stirring is achieved with a very small gas flow, it becomes economically advantageous to choose an inert gas, such as argon or helium, which, besides its stirring action, will be useful as a flushing agent, for removing from the metal gases, such as hydrogen or nitrogen, and for protecting the bath surface against oxidation and nitride formation at the contact of the atmosphere. These are also effective, when using the present apparatus, to protect the bath surface against the reabsorption of hydrogen from the water vapour which is always present to some extent in the atmosphere. Another favorable consequence of using a very small gas flow is that heat losses are kept down. The feature, according to which the depth of the bath is relatively large, is also quite favorable in this respect. In one of the tests mentioned in the foregoing, where argon was blown into a bath of 3 tons of steel at the rate of 12 liters/minute/ton, through a porous plug of 10 centimeters diameter, the bath temperature, which was initially 1560° C., still attained 1460° C. after 15 minutes of stirring, no heat having been supplied to the bath during this operation. In this test, the diameter of the bath surface was approximately 80 centimeters, so that the ratio plug-area to bath-area was approximately 1/64. For larger ladle sizes, this ratio can be further decreased, as already indicated, for instance down to 1/100 for a 5 ton ladle and even less, for example 1/250, for ladles larger than the 10 ton size. In tests conducted on normal industrial scale, plugs of 10 centimeters top diameter have been used successfully for treating batches up to 15 tons, and would appear appropriate in 20 ton ladles designed according to the present invention, with a gas flow of about 5 to 8 liters per minute per ton. More recent tests carried out on pig iron batches of approximately 17 tons have shown that the temperature drop did not exceed one degree C per minute of blowing.

Preheating the gas is not recommended, since the thermal expansion of the gas within the molten bath appears to contribute to the stirring, and since the quantity of heat absorbed from the bath by the gas is relatively very small.

Among possible uses of the present method and apparatus, mention will be made of the incorporation to molten metals of agents, such as magnesium or boron, which are highly reactive to oxygen and/or nitrogen. Blowing argon or helium into the molten metal,

according to the procedure outlined, just before and while adding these agents to the metal facilitates their dispersion therein and protects them substantially against oxidation and/or nitride formation.

It is to be noted that, since methodical stirring is obtained by means of the present invention, the role of diffusion, in metallurgical operations conducted according to the principles herein set forth, will be restricted to short-distance action, and exchanges or reactions within the fused bath will be completed in much less time owing to the constant renewal of the exchange surfaces, achieved when using the device of the present invention.

What we claim is:—

1. Ladle for the treatment of molten metals by gases, said ladle having a refractory lining, the bottom of which comprises a porous portion substantially flush with the rest of said lining, and means to blow gas through said porous portion, characterized by the ratio (a) between the ladle depth at its normal filling level and the ladle's inner diameter at said level being comprised between 1 and 1.8, and the ratio (*b*) between the porous area *s* in the ladle bottom and the area S of the ladle's inner section at its normal filling level complying with the relation:

$$0.32 \log S + 0.39 < \log s < 0.67 \log S - 0.14$$

2. Ladle according to claim 1, in which the ratio (*a*) is comprised between 1.2 and 1.6, and the ratio (*b*) complies with the relation:

$$0.475 \log S < \log s < 0.475 \log S + 0.40.$$

3. Ladle according to claim 1, in which the permeability of the porous portion is comprised between 50 and 200 liters of air issuing at room temperature and normal atmospheric pressure, per minute, per square decimeter of exposed porous area, and per kilogram per square centimeter upstream pressure.

4. Ladle according to claim 1, for the treatment of ferrous metals, in which the porous portion is a removable silicon carbide plug.

5. Ladle according to claim 4, in which the silicon carbide plug is sealed to the ladle lining by means of chromium-oxide base cement containing a small amount of bentonite and sodium silicate.

6. A method of desulphurizing molten ferrous metals, using a ladle according to claim 1, characterized by the steps of first charging a desulphurizing slag in the solid state into the empty ladle, and subsequently charging molten metal into said ladle, while blowing gas through the bottom of said ladle, thereby mixing said slag with the molten metal and activating the process of desulphurizing by assisting the elimination of CO as it is formed.

7. A method of desulphurizing molten ferrous metals, according to claim 6, characterized by the desulphurizing slag being a blast-furnace slag.

8. A method of de-oxidizing molten steel, using a ladle according to claim 1, and adding a small amount of carbon to the steel before pouring, characterized by the step of blowing an inert gas through the bottom of the ladle into the molten steel, thereby activating the dispersion of carbon into the steel and lowering the partial pressure of CO as it is formed.

9. A method of lowering the silicon content of molten ferrous metals, using a ladle according to claim 1, characterized by the step of blowing an inert gas through the bottom of the ladle into the molten metal, while the silicon in said metal becomes oxidized into silicon monoxide, thereby lowering the partial pressure of gaseous SiO and assisting the elimination thereof.

10. The improved ladle as hereinbefore described and illustrated with reference to Figure 1 of the accompanying drawings.

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2 SHEETS
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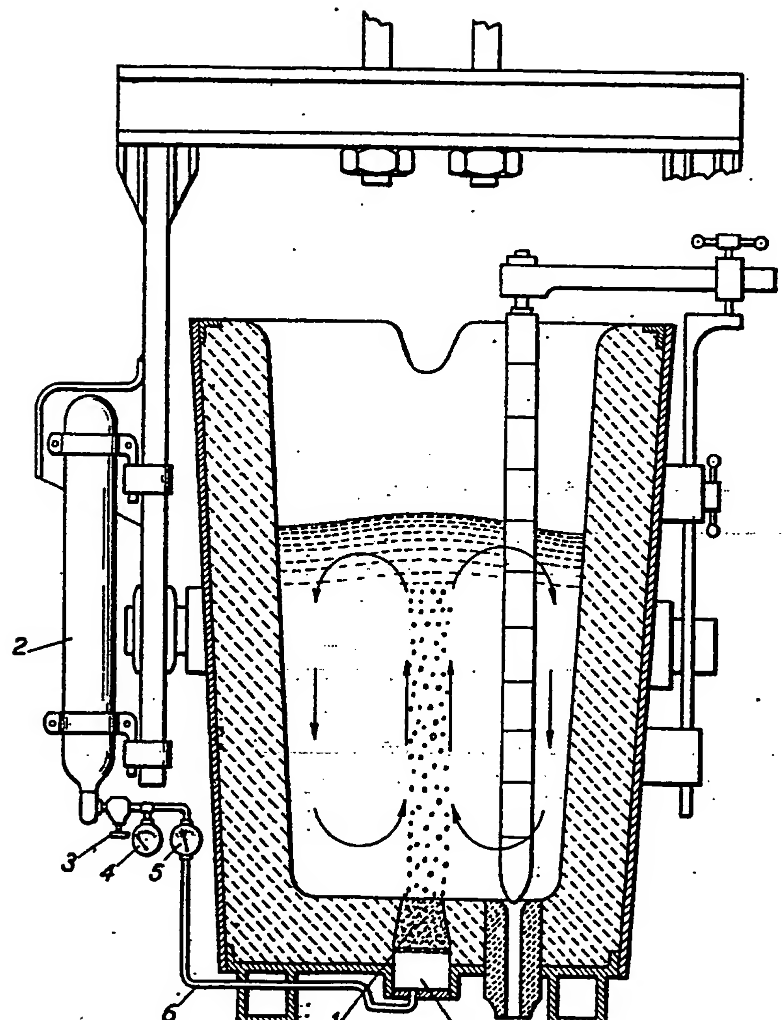
SHEET 1

Fig. I



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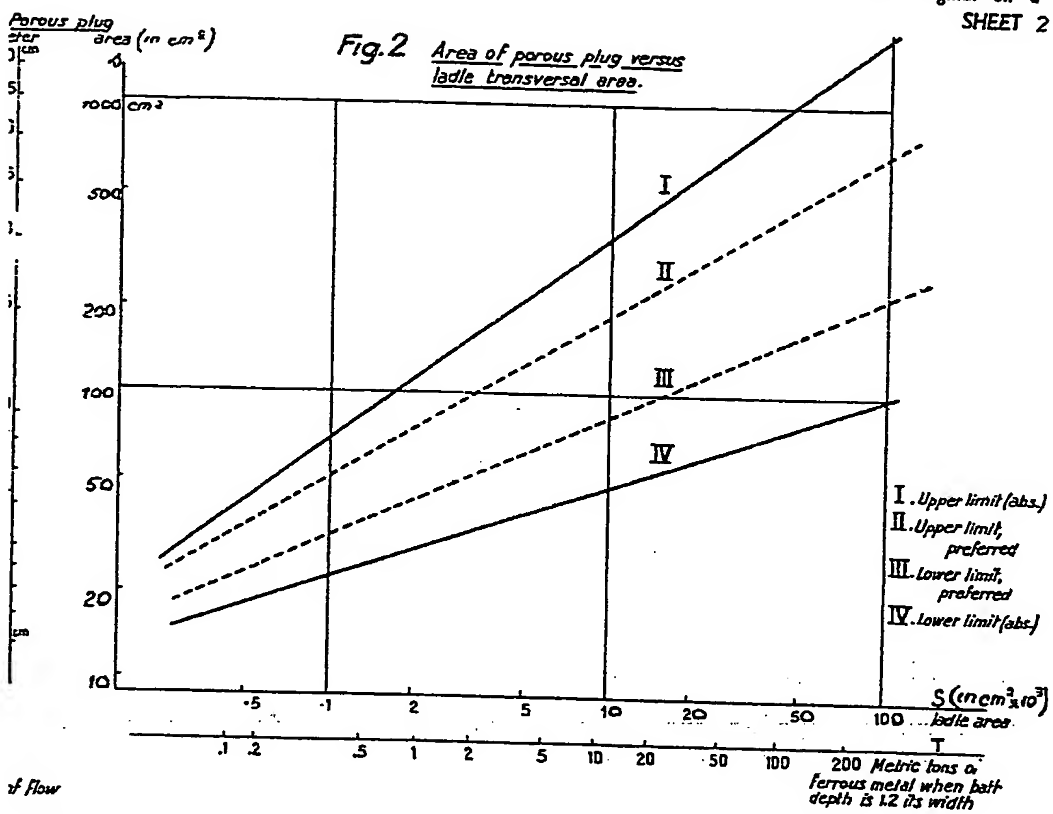
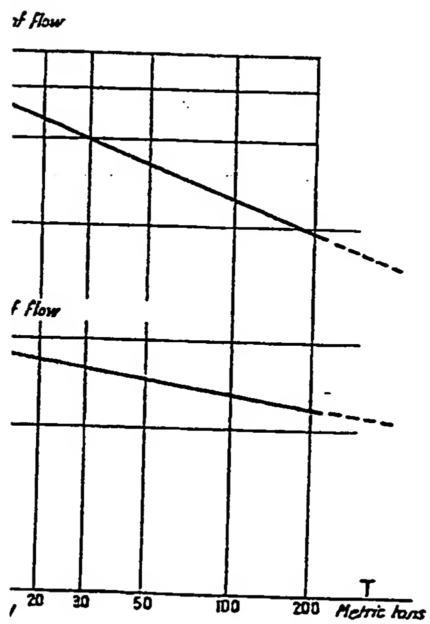
SHEET 2

Fig. 2 Area of porous plug versus ladle transversal area.





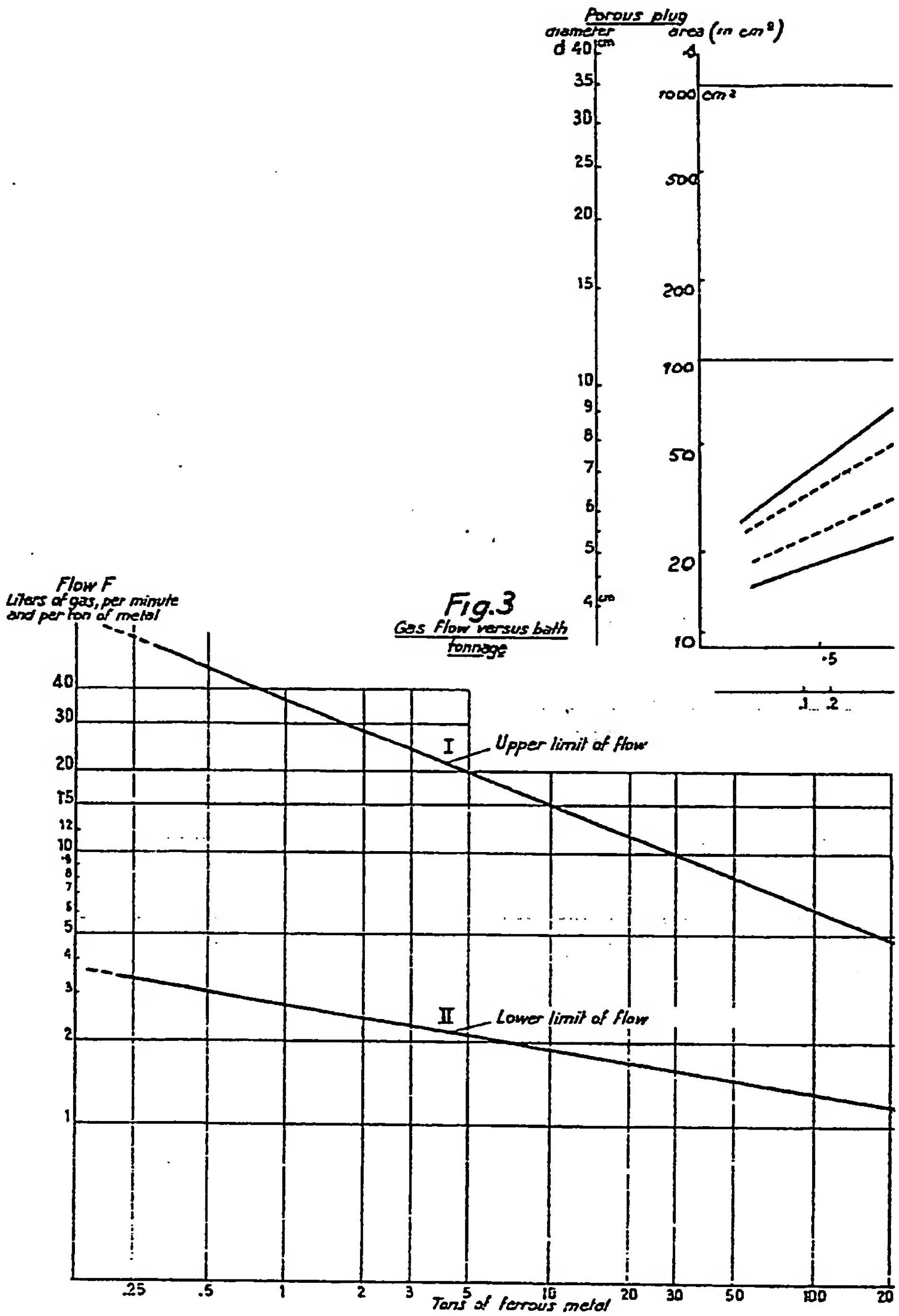


Fig.3
Gas Flow versus bath tonnage

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SHEET 2

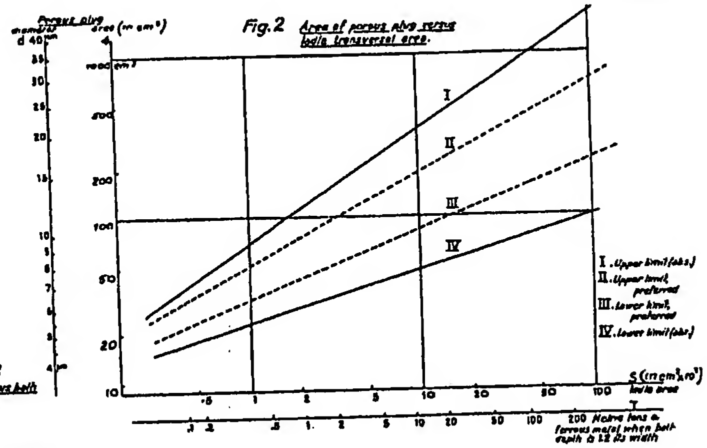

Fig. 2 Area of porous plug versus ladle transversal area.

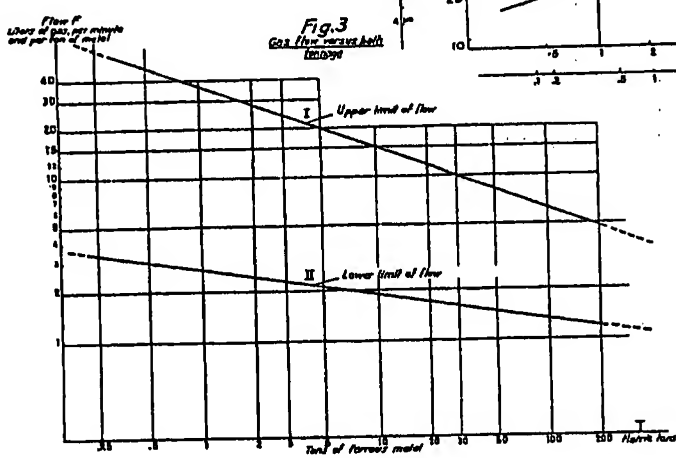

Fig. 3 Gas flow versus ladle tonnage